

Structure and characterisation of a novel 3-D Ba(II)–MOF based on the {Ba₄O₇} core

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A novel three-dimensional barium metal–organic framework [Ba₃(btc)₂(H₂O)₄].0.5H₂O (H₃btc = 1,3,5-benzenetricarboxylic acid) has been synthesised under hydrothermal conditions, and characterised by single-crystal X-ray structure determination, thermogravimetric analysis, X-ray powder diffraction, IR, and photoluminescence studies. The volume of the tunnel formed by the two-dimensional layers is 341.9 Å³ per unit cell using PLATON based on the crystal structures, comprising 14.3% of the crystal volume 2387.2 Å³. The solid-state fluorescence measurement of this compound at room temperature reveals a fluorescent emission band at 454.5 nm under the excitation of 337 nm, assigned to a charge-transfer transition.

Keywords: X-ray structure, Ba(II)–btc MOF, {Ba₄O₇} core, fluorescence

Recently, we have investigated the design and synthesis of multi-dimensional metal–organic frameworks (MOFs). This is not only due to their complicated structural diversity but also their potential applications in catalysis, gas adsorption, magnetism, luminescence, molecular sensing and separation, and molecular recognition.¹ Organic polycarboxylate ligands, such as rigid 1,3,5-benzenetricarboxylate, phosphonates adorned with multi-carboxyl groups, and sulfonates containing carboxyl groups, *etc.*, as multi-dentate O/N-donor ligands, have been extensively used in the preparation of such MOFs with multi-dimensional networks and interesting properties.^{2–4} Based on diversified structures *via* partial or complete deprotonation of carboxyl groups, MOFs with 1,3,5-benzenetricarboxylic acid (H₃btc) have been widely studied to date.⁵ Barium(II) possesses a large radius (Pauling ion radius, 1.35 Å), a variable stereochemical activity, and a flexible coordination environment. These properties make it a flexible metal ion, which provides unique opportunities for the construction of novel metal–organic frameworks (MOFs).^{6,7}

However, coordination polymers of alkaline earth metals have been very rare, and reports on barium-based MOFs with H₃btc are especially uncommon.⁸ One direction of gas storage studies is to build MOFs based on reduced density for an enhancement of gravimetric storage capacity. MOFs derived from main group metals, such as Ba²⁺, may play an important role in this field.⁹ Therefore, our research has focused on the synthesis of MOFs based on barium. Here we describe the structure of a three-dimensional (3-D) novel barium carboxylate, namely [Ba₃(btc)₂(H₂O)₄].0.5H₂O **1**, and its fluorescent properties.

Results and discussion

Single-crystal X-ray diffraction analysis reveals that compound **1** possesses a 3-D architecture, in which the asymmetric unit (Fig. 1) contains three crystallographically unique Ba(II) ions, two btc³⁻ ligands, one bridging water molecule, three terminal water molecules and one lattice water molecule. Crystallographic data and structural refinements are summarised in Table 1.

In the structure of **1**, the Ba(1) ion is seven-coordinated with four O atoms from four different carboxylate groups [O(3), O(4A), O(5), O(6)], two terminal O atoms [O(1), O(2)] and one bridging O atom [O(7)] from three coordinated water molecules. The coordination geometry around the Ba(1) ion can be described as a singly-capped octahedron. Ba(2) and

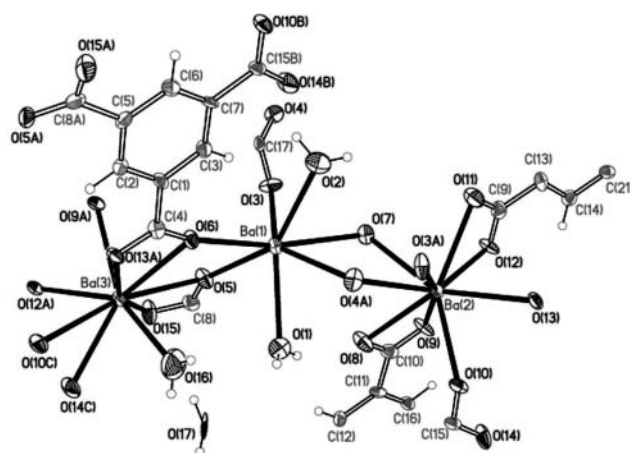


Fig. 1 ORTEP view of **1** showing the atom-labeling scheme (40% thermal ellipsoids).

Table 1 Crystal data and structure refinement for **1**

Empirical formula	C ₁₈ H ₁₃ Ba ₃ O _{16.50}
Formula weight	905.30
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>Pna2(1)</i>
Unit cell dimensions	<i>a</i> = 13.2452(13) Å <i>b</i> = 10.2291(10) Å <i>c</i> = 17.6191(18) Å
Volume	2387.1(4) Å ³
<i>Z</i>	4
Calculated density	2.519 Mg m ⁻³
Absorption coefficient	4.977 mm ⁻¹
<i>F</i> (000)	1684
Theta range for data collection	2.3°–26.00°
Limiting indices	–16 ≤ <i>h</i> ≤ 14, –11 ≤ <i>k</i> ≤ 12, –19 ≤ <i>l</i> ≤ 21
Reflections collected / unique	12227 / 3842 [<i>R</i> (int) = 0.0430]
Completeness to theta = 25.00	99.9 %
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	3842 / 7 / 344
Goodness-of-fit on <i>F</i> ²	1.068
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ¹ = 0.0281, <i>wR</i> ² = 0.065
<i>R</i> indices (all data)	<i>R</i> ¹ = 0.0321, <i>wR</i> ² = 0.0672
Extinction coefficient	0.00422(15)
Largest diff. peak and hole	0.694 and –0.533 e. Å ⁻³

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Table 2 Bond lengths [Å] and angles [°] for **1**

Ba(1)–O(5)	2.689(4)	Ba(2)–O(9)	2.850(5)
Ba(1)–O(6)	2.714(5)	Ba(2)–O(7)	2.868(6)
Ba(1)–O(2)	2.720(6)	Ba(2)–O(3)#1	2.917(5)
Ba(1)–O(4)#1	2.726(5)	Ba(3)–O(12)#2	2.721(6)
Ba(1)–O(3)	2.782(5)	Ba(3)–O(9)#2	2.733(6)
Ba(1)–O(1)	2.828(6)	Ba(3)–O(16)	2.751(8)
Ba(1)–O(7)	2.917(5)	Ba(3)–O(14)#3	2.752(6)
Ba(2)–O(10)	2.711(5)	Ba(3)–O(15)	2.787(6)
Ba(2)–O(4)#1	2.735(5)	Ba(3)–O(5)	2.800(7)
Ba(2)–O(13)	2.793(5)	Ba(3)–O(13)#3	2.802(5)
Ba(2)–O(11)	2.795(5)	Ba(3)–O(6)	2.986(5)
Ba(2)–O(12)	2.808(5)	Ba(3)–O(10)#3	3.046(5)
Ba(2)–O(8)	2.838(5)		
O(5)–Ba(1)–O(6)	73.88(19)	O(5)–Ba(1)–Ba(3)	35.57(14)
O(5)–Ba(1)–O(2)	144.84(17)	O(6)–Ba(1)–Ba(3)	39.89(10)
O(6)–Ba(1)–O(2)	94.69(18)	O(2)–Ba(1)–Ba(3)	131.30(14)
O(5)–Ba(1)–O(4)#1	140.26(15)	O(4)#1–Ba(1)–Ba(3)	127.42(12)
O(6)–Ba(1)–O(4)#1	109.71(16)	O(3)–Ba(1)–Ba(3)	99.51(12)
O(2)–Ba(1)–O(4)#1	74.86(18)	O(1)–Ba(1)–Ba(3)	73.60(11)
O(5)–Ba(1)–O(3)	74.96(15)	O(7)–Ba(1)–Ba(3)	150.65(11)
O(6)–Ba(1)–O(3)	111.06(16)	O(5)–Ba(1)–Ba(2)	130.27(15)
O(2)–Ba(1)–O(3)	78.75(18)	O(6)–Ba(1)–Ba(2)	142.30(11)
O(4)#1–Ba(1)–O(3)	132.62(16)	O(2)–Ba(1)–Ba(2)	78.55(13)
O(5)–Ba(1)–O(1)	72.21(16)	O(4)#1–Ba(1)–Ba(2)	32.62(11)
O(6)–Ba(1)–O(1)	95.01(17)	O(3)–Ba(1)–Ba(2)	103.96(11)
O(2)–Ba(1)–O(1)	142.80(19)	O(1)–Ba(1)–Ba(2)	71.96(11)
O(4)#1–Ba(1)–O(1)	68.05(16)	O(7)–Ba(1)–Ba(2)	36.91(12)
O(3)–Ba(1)–O(1)	129.77(17)	Ba(3)–Ba(1)–Ba(2)	145.486(13)
O(5)–Ba(1)–O(7)	115.53(18)	O(10)–Ba(2)–O(4)#1	98.54(16)
O(6)–Ba(1)–O(7)	168.33(15)	O(10)–Ba(2)–O(13)	68.65(18)
O(2)–Ba(1)–O(7)	73.63(17)	O(4)#1–Ba(2)–O(13)	126.59(15)
O(4)#1–Ba(1)–O(7)	68.05(16)	O(10)–Ba(2)–O(11)	145.15(18)
O(3)–Ba(1)–O(7)	67.09(16)	O(4)#1–Ba(2)–O(11)	105.12(17)
O(1)–Ba(1)–O(7)	94.59(16)	O(13)–Ba(2)–O(11)	76.70(17)
O(10)–Ba(2)–O(12)	118.15(16)	O(16)–Ba(3)–O(5)	87.75(19)
O(4)#1–Ba(2)–O(12)	142.90(16)	O(14)#3–Ba(3)–O(5)	128.47(17)
O(13)–Ba(2)–O(12)	75.90(17)	O(15)–Ba(3)–O(5)	46.82(14)
O(11)–Ba(2)–O(12)	46.36(17)	O(12)#2–Ba(3)–O(13)#3	112.25(16)
O(10)–Ba(2)–O(8)	76.77(17)	O(9)#2–Ba(3)–O(13)#3	74.25(17)
O(4)#1–Ba(2)–O(8)	74.05(16)	O(16)–Ba(3)–O(13)#3	75.3(2)
O(13)–Ba(2)–O(8)	141.46(17)	O(16)–Ba(3)–O(15)	106.8(2)
O(11)–Ba(2)–O(8)	134.1(2)	O(14)#3–Ba(3)–O(15)	95.68(17)
O(12)–Ba(2)–O(8)	107.56(16)	O(12)#2–Ba(3)–O(5)	118.43(14)
O(10)–Ba(2)–O(9)	82.90(16)	O(9)#2–Ba(3)–O(5)	86.57(16)
O(4)#1–Ba(2)–O(9)	117.92(16)	O(14)#3–Ba(3)–O(13)#3	104.80(16)
O(13)–Ba(2)–O(9)	111.70(16)	O(15)–Ba(3)–O(13)#3	158.46(15)
O(11)–Ba(2)–O(9)	107.22(16)	O(5)–Ba(3)–O(13)#3	112.88(15)
O(12)–Ba(2)–O(9)	65.32(18)	O(12)#2–Ba(3)–O(6)	140.11(15)
O(8)–Ba(2)–O(9)	45.62(16)	O(9)#2–Ba(3)–O(6)	73.45(16)
O(10)–Ba(2)–O(7)	141.19(16)	O(16)–Ba(3)–O(6)	71.30(18)
O(4)#1–Ba(2)–O(7)	68.65(15)	O(14)#3–Ba(3)–O(6)	135.4(2)
O(13)–Ba(2)–O(7)	148.62(14)	O(15)–Ba(3)–O(6)	114.74(15)
O(11)–Ba(2)–O(7)	72.49(17)	O(5)–Ba(3)–O(6)	68.19(14)
O(12)–Ba(2)–O(7)	78.62(16)	O(13)#3–Ba(3)–O(6)	44.74(15)
O(8)–Ba(2)–O(7)	64.56(17)	O(12)#2–Ba(3)–O(10)#3	76.02(16)
O(9)–Ba(2)–O(7)	72.78(16)	O(9)#2–Ba(3)–O(10)#3	106.96(15)
O(10)–Ba(2)–O(3)#1	91.16(16)	O(16)–Ba(3)–O(10)#3	75.93(19)
O(4)#1–Ba(2)–O(3)#1	46.37(14)	O(14)#3–Ba(3)–O(10)#3	44.54(16)
O(13)–Ba(2)–O(3)#1	81.18(15)	O(15)–Ba(3)–O(10)#3	137.56(15)
O(11)–Ba(2)–O(3)#1	87.13(16)	O(5)–Ba(3)–O(10)#3	163.67(14)
O(12)–Ba(2)–O(3)#1	131.49(15)	O(13)#3–Ba(3)–O(10)#3	63.97(16)
O(8)–Ba(2)–O(3)#1	116.79(16)	O(6)–Ba(3)–O(10)#3	106.30(14)
O(9)–Ba(2)–O(3)#1	162.30(15)	Ba(1)–O(3)–Ba(2)#11	137.12(19)
O(7)–Ba(2)–O(3)#1	102.87(15)	Ba(1)#11–O(4)–Ba(2)#11	114.88(17)
O(12)#2–Ba(3)–O(9)#2	68.09(19)	Ba(1)–O(5)–Ba(3)	110.5(2)
O(12)#2–Ba(3)–O(16)	143.25(18)	Ba(1)–O(6)–Ba(3)	104.45(16)
O(9)#2–Ba(3)–O(16)	143.8(2)	Ba(2)–O(7)–Ba(1)	105.44(18)
O(12)#2–Ba(3)–O(14)#3	74.44(18)	Ba(3)#5–O(9)–Ba(2)	106.38(18)
O(9)#2–Ba(3)–O(14)#3	138.25(18)	Ba(2)–O(10)–Ba(3)#9	102.64(17)
O(16)–Ba(3)–O(14)#3	68.94(19)	Ba(3)#5–O(12)–Ba(2)	107.89(18)
O(12)#2–Ba(3)–O(15)	79.35(16)	Ba(2)–O(13)–Ba(3)#9	107.05(17)
O(9)#2–Ba(3)–O(15)	94.91(17)		

Symmetry transformations used to generate equivalent atoms:

#1 $x+1/2, -y+3/2, z$ #2 $-x, -y+1, z+1/2$ #3 $-x+1/2, y-1/2, z+1/2$ #4 $-x+1/2, y+1/2, z+1/2$ #5 $-x, -y+1, z-1/2$ #6 $x, y-1, z$ #7 $x, y+1, z$
 #8 $-x+1/2, y-1/2, z-1/2$ #9 $-x+1/2, y+1/2, z-1/2$ #10 $-x, -y+2, z+1/2$ #11 $x-1/2, -y+3/2, z$ #12 $-x, -y+2, z-1/2$

Ba(3) are nine-coordinate and the coordination geometry around the Ba(II) ions can be described as a distorted, tri-capped trigonal prism arrangement. The coordination sphere of Ba(2) is composed of eight carboxylate oxygen atoms from five different carboxylate groups [O(3A), O(4A), O(8), O(9), O(10), O(11), O(12), O(13)] and one bridging oxygen atom from one coordinated water molecule [O(7)]. The coordination sphere of Ba(3) is composed of eight carboxylate oxygen atoms from five different carboxylate groups [O(6), O(13A), O(5), O(15), O(10C), O(14C), O(9A), O(12A)] and one terminal oxygen atom from one coordinated water molecule [O(16)]. The bond lengths of the Ba–O_{carboxylate} bonds range from 2.689(4) to 3.046(5) Å with the mean of 2.802(4) Å and the Ba–O_w bonds from 2.720(6) to 2.917(5) Å with the mean of 2.804(6) Å, which compare well with the average values determined from those of reported Ba(II)–btc compound.⁸ Selected bond lengths and angles are listed in Table 2.

Both crystallographic unique btc³⁻ molecules bonding with the Ba(II) ions adopt the same coordination modes ($\mu_7:\eta^4\eta^3\eta^3$) in the structure (Fig. 2). There are two types of coordination for the carboxyl groups: (i) in the $\mu_3:\eta^4$ mode, chelating with three Ba(II) ions, including two carboxyl groups [μ_2 -O(3), μ_2 -O(4) and μ_2 -O(6), μ_2 -O(13)]; (ii) in the $\mu_2:\eta^3$ mode, chelating with two Ba(II) ions, including four carboxyl groups [μ_2 -O(5), O(15); O(8), μ_2 -O(9); O(11), μ_2 -O(12) and μ_2 -O(10), O(14)].

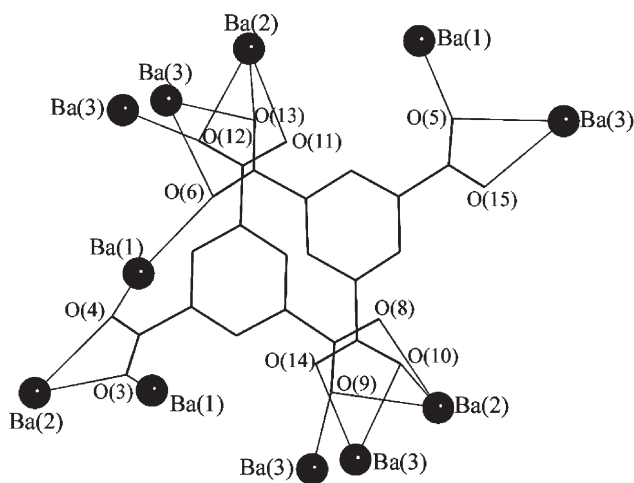


Fig. 2 Coordination modes of the carboxyl groups in 1.

Compound 1 contains a {Ba₄O₇} core (Fig. 3) that can be described as an edge-shared tetranuclear polyhedron with seven μ_2 -O atoms. The tetranuclear core {Ba₄O₇}, as a basic structural unit, is joined together by the Ba(2) ion to form a 1-D Ba–O inorganic chain structure along the *a*-axis. The organic btc³⁻ ligands hang on both sides of the one-dimensional (1-D) chain (Fig. 3). The Ba(1) and Ba(3) ions, between the two adjacent parallel inorganic chains, are joined together by the oxygen atoms [μ_2 -O(5) and μ_2 -O(6)] of the ligand btc³⁻, leading to a two-dimensional (2-D) inorganic layer framework in the *ac* plane (Fig. 4). Three types of multi-membered rings, a four-membered ring [–Ba–O–Ba–O–], an eight-membered ring [–Ba–O–Ba–O–]₂ and a 20-membered ring [–Ba–O–Ba–O–]₅, are assembled in the structure.

The above 2-D layers are further linked together *via* the oxygen atoms [μ_2 -O(5) and μ_2 -O(6)] to give rise to a 3-D MOF structure. The lattice water molecule [O(17)] occupies the voids between layers and is involved in hydrogen bonds. Due to the existence of the water molecules and organic ligand btc³⁻, few voids are observed in the overall 2-D crystalline lattice. After the removal of the water molecules, one-dimensional channels defined by 2-D inorganic layer are observed stacked along the *b*-axis (Fig. 5). Accordingly, the volume of the tunnel formed by the 2-D layers is 341.9 Å³ per unit cell using PLATON based on the crystal structures, comprising 14.3% of the crystal volume 2387.2 Å³.¹⁰

Regarding the Ba(II) ion as node, the 2-D layer actually bring out the lozenge fish-netted 2-D topological layout. It should be noted that the 2-D lozenge fish-netted structure is the first example for the Ba(II) ion, based on a Cambridge Structure Database (CSD) search until now (May, 2010).¹¹ By weaving together the infinite lozenge-like layers, a 3-D fish-netted topological network is built through the linker Ba(1)–Ba(3) (see Fig. S1, deposited in the ESI).

In addition, there are many hydrogen bonds (O–H...O) in 1. These hydrogen bonds are formed between the ligand btc³⁻ [O(8), O(11), O(12), O(14), O(15)] and the water molecules [O(1), O(2), O(16), O(17)], and further reinforce the 3-D structure. Hydrogen bonds and angles are given in Table 3.

XRD and TG-DTA study

The powder XRD pattern of 1 indicates that the as-synthesised product is a new material, and the pattern is entirely consistent with the simulated one from the single-crystal X-ray diffraction [see Fig. S2, deposited in the Electronic Supplementary Information (ESI)].

The combined TG–DTA analysis [see Fig. S3, deposited in the ESI] shows two major weight losses. The first mass loss of

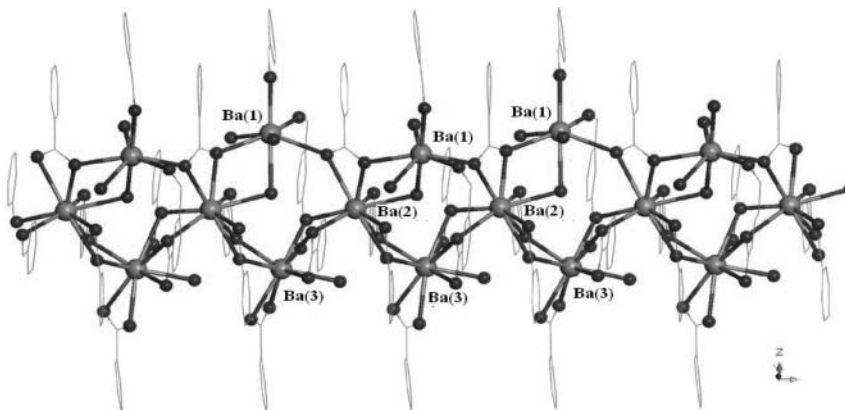


Fig. 3 View of 1-D inorganic chain containing the {Ba₄O₇} core along the *a*-axis.

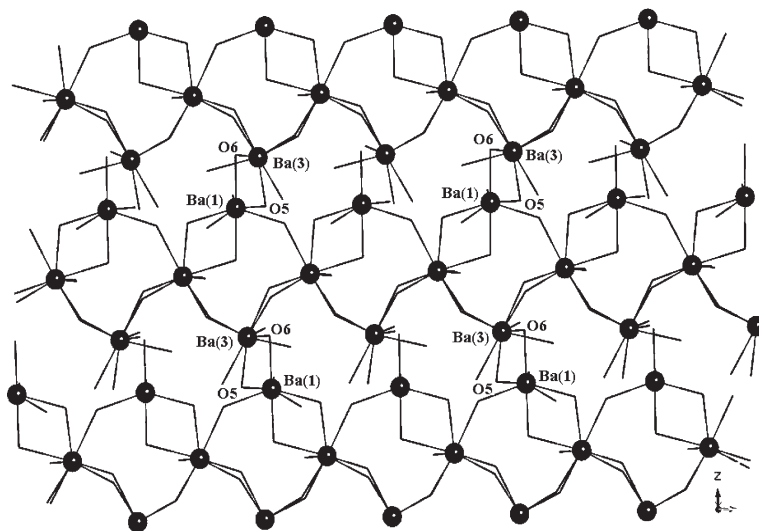


Fig. 4 2-D layer built from the inorganic chains in the *ac* plane. The lattice water molecules are omitted for clarity.

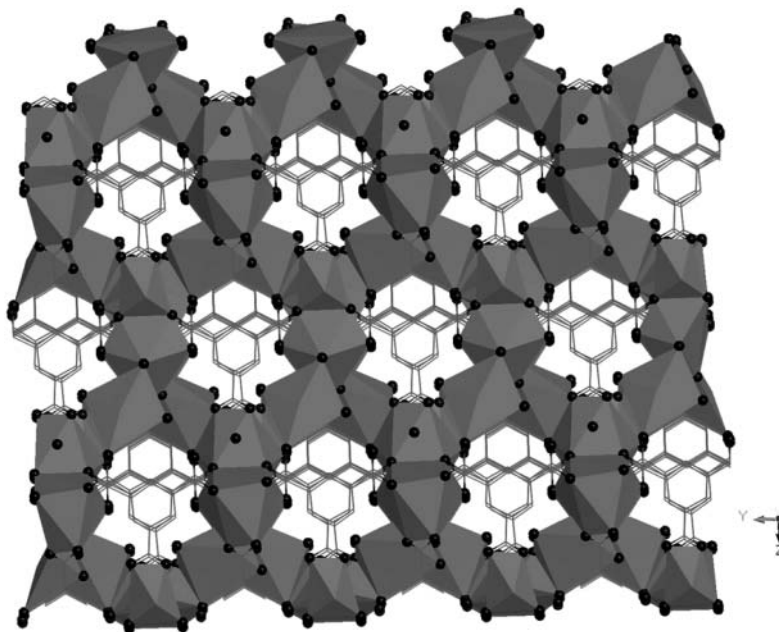


Fig. 5 3-D porous network created from 2-D inorganic layers stacking along the [010] direction.

8.80% from 100 to 210 °C, with a weak endothermic peak centred at 185 °C, corresponds to the loss of one lattice water molecule and four coordinated water molecules (Calcd 8.73%). The broad range required to lose the water molecules is attributed to the various coordination interactions. The second mass loss of about 25.84% (Calcd 25.89%), in the range of 430–600 °C, can be assigned to the pyrolysis of the organic ligand. The exothermic peak centred at 547 °C indicates structural changes. The final thermal decomposition residue at 800 °C is BaCO₃, which possesses a mass of 65.36% (Calcd 65.38%).

Photoluminescent properties

We investigated the solid-state photoluminescent properties of **1** at room temperatures (see Fig. S4, deposited in the ESI). Free H₃BTC shows a main emission in the visible region at 390 nm and a shoulder peak 370 nm ($\lambda_{\text{excitation}} = 344$ nm),

whereas compound **1** shows an emission band at 454.5 nm ($\lambda_{\text{excitation}} = 337$ nm). Test results show that an emission maximum at 454.5 nm may arise from a charge-transfer transition, rather than the $\pi^* \rightarrow n$ transition of the organic ligand.¹² The results suggest that the unexpected photoluminescent properties of the product is largely dependent on the assembly structure and the coordination between the Ba(II) ion and the organic ligand.

Experimental

All chemical reagents were obtained from commercial sources and used without further purification. Elemental analyses were conducted on a Perkin-Elmer 2400 LC II elemental analyser. IR spectra were obtained on a Nicolet Impact 410 FI-IR spectrometer as KBr pellets in the 400–4000 cm⁻¹ region. Thermo-gravimetric (TG) and differential thermal analysis (DTA) were performed on a TG/SDTA851e analyser

Table 3 Hydrogen bond lengths [Å] and angles [°] for **1**

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
O(1)–H(11)...O(8)	0.87	2.02	2.714(9)	135.7
O(1)–H(12W)...O(15)#13	0.89	1.96	2.824(9)	165.5
O(2)–H(21)...O(17)#7	0.85	2.04	2.837(12)	155.9
O(2)–H(22)...O(14)#4	0.92	2.19	2.725(9)	116.5
O(16)–H(161)...O(12)#3	0.85	2.22	2.994(11)	150.8
O(17)–H(171)...O(11)#6	0.84	2.27	2.790(13)	120.5
O(17)–H(173)...O(1)	0.90	2.45	3.211(12)	142.2
O(16)–H(162)...O(17)	0.91	2.35	3.117(14)	141.4

Symmetry transformations used to generate equivalent atoms:

#1 $x+1/2, -y+3/2, z$ #2 $-x, -y+1, z+1/2$ #3 $-x+1/2, y-1/2, z+1/2$ #4 $-x+1/2, y+1/2, z+1/2$ #5 $-x, -y+1, z-1/2$ #6 $x, y-1, z$ #7 $x, y+1, z$ #8 $-x+1/2, y-1/2, z-1/2$ #9 $-x+1/2, y+1/2, z-1/2$ #10 $-x, -y+2, z+1/2$ #11 $x-1/2, -y+3/2, z$ #12 $-x, -y+2, z-1/2$ #13 $x+1/2, -y+1/2, z$

by Mettler-Toledo Co. of Switzerland in an atmospheric environment at a heating rate of 10 °C/min. Emission and excitation spectra were recorded on a PerkinElmer LS 55 fluorescence spectrometer. The powder X-ray diffraction (XRD) patterns were collected on an ARL X'TRA diffractometer using graphite-monochromated CuK α radiation ($\lambda = 1.5418$ Å) in the angular range $2\theta = 4^\circ$ – 40° with stepping size of 0.02° and counting time of 4 s per step.

Synthesis of [Ba₃(btc)₂(H₂O)₄]-0.5H₂O **1**

A mixture of BaCl₂·2H₂O (0.195 g, 0.8 mmol), H₃btc (0.042 g, 0.2 mmol) and deionized water (10.0 mL, 555 mmol) was sealed in a 15 mL Teflon-lined stainless steel autoclave. The initial pH value of the solution was adjusted to about 8.0, then it was heated at 170 °C for 100 h. The final pH value was 7.0. The colourless, crystalline **1** was collected by vacuum filtration, washed thoroughly with deionized water and dried in air (yield 65% based on barium). Anal. for Calcd C₁₈H₁₃Ba₃O_{16.50}: C, 23.86; H, 1.43. Found: C, 23.79; H, 1.35%. IR data (cm⁻¹): 3404 (m), 3176 (w), 3019 (w), 2912 (w), 1618 (s), 1546 (s), 1429 (s), 1369 (s), 1205 (w), 1105 (m), 889 (w), 817 (w), 765 (w), 723 (m), 595 (w), 472 (m) (see Fig. S5 deposited in the ESI).

X-ray data collection and structure determinations

Intensity data were collected on a Bruker SMART APEX II diffractometer equipped with a graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 293 K using the ω - 2θ scan technique. The structure was solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELXL-97. A total of 12227 reflections were collected, of which 3842 ($R_{\text{int}} = 0.043$) were unique. All non-hydrogen atoms were located from the initial solution and refined with anisotropic thermal parameters. The position of hydrogen atoms were located by calculated geometrically and their contributions in structural factor calculations were included.

CCDC 765594 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Conclusions

In summary, we have successfully synthesised a novel 3-D Ba(II)-btc compound **1** under hydrothermal conditions. Compound **1** displays a 2-D, lozenge fish-netted inorganic layer architecture with three types of multi-membered rings around

the Ba(II) ion. The Ba(II) ions are nine and seven-coordinate, respectively, leading to the formation of a 3-D porous structure, occupied by the organic ligand and the lattice water molecules. Solid-state fluorescence measurements of **1** at room temperature reveal a fluorescent emission band at 454.5 nm under the excitation of 337 nm, likely caused by a charge-transfer transition.

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Electronic Supplementary Information

Figures S1, S2, S3, S4 and S5 have been deposited in the ESI available through stl.publisher.intgentaconnect.com/content/stl/jcr/supp-data.

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